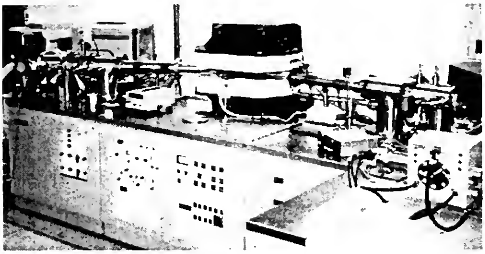
1998 Annual Report

RESEARCH AND DEVELOPMENT



Laboratory Services Branch
Ontario Ministry of Environment
March, 1999

Front Cover Photographs (Clockwise From Top Left)

A. High Resolution Hybrid Mass Spectrometer Equipped for LC/MS Operation
B. LSB Staff Show Electrospray Interface for Bench-Top LC/MS
C. Staff of Ministry of Environment, Laboratory Services Branch
D. Registration for LSB Seminar on Polynuclear Aromatic Hydrocarbons

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Research and Development

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Overview

The Laboratory Services Branch (LSB) continues to restructure and evolve away from routine testing towards support of core ministry functions and reference centre activities. This process was especially well illustrated in the past year as the LSB began development of its first real-matrix certified environmental reference material (CRM). This is an important step in our ability to deliver environmental analytical reference services, because CRMs are essential to method development, laboratory evaluation, and quality control studies. Although many CRMs have become commercially available in recent years, there still exists a huge gap between the CRMs available and the CRMs which are needed.

Other reference centre activities have continued to grow in size and scope during 1998. Some 60 delegates registered to attend a PAH seminar in which the issues of toxicity, sources, analytical methods, and contamination case studies were covered by LSB and Operations Division staff. Several delegates were from the private sector. Such seminars and workshops are specifically directed to the end-user of our analytical services, and contribute to the upgrading of skills for working professionals, and improved analytical data quality. Other activities included a continuation of the LSB seminar series, and several seminars sponsored by commercial laboratory suppliers.

In R&D studies, significant improvements were made to the determination of congener-specific PCBs, total petroleum hydrocarbons, metals in air, and taste and odour compounds. Further progress was made in the application of Liquid Chromatography/Mass Spectrometry to aqueous sample types. Technologies such as microwave-assisted extractions and fast gas chromatography were studied to speed up the analytical process to improve productivity, lower the unit cost of analysis, and generate results for LSB customers more rapidly. It may take several years to fully integrate such technologies into LSB methods, but the savings in cost and turnaround time should be substantial.

For further information on any of the projects described in this report, readers are directed to the Study Leader, or to the Author:

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A. New Applications of Technology

Introduction

Liquid Chromatography/Mass Spectrometry (LC/MS) R&D has increased in importance with the acquisition of a new bench-top LC/MS system by LSB. Now that systems are available commercially that can achieve much better detection limits than were possible only a few years ago, LC/MS may now be the technique of choice for certain applications, such as pesticides in aqueous sample types. LC/MS also allows us to measure some classes of pollutants that are not readily amenable to GC/MS determination, and which are therefore poorly characterized in the Ontario environment. A second relatively new technology – Fast Gas Chromatography – promises to have an even greater impact on analytical operations, as sample analysis times for some organics can be lowered 5-10 fold with no loss in the resolution of key components.

An ongoing study on the use of microwave ovens to improve extraction times of various analytes from solid sample types was continued. Although many studies of the use of microwave ovens for such applications have been reported by others, and commercially manufactured equipment for this purpose is available, this technique is still far from routine. Specific parameters must be developed for each sample type, and a specific microwave extraction method developed for the soil samples from one location may not be effective for soils from a different area. However, the potential benefits of this approach are great, for both organic and inorganic analytes. Other technologies reported herein for the analysis of difficult environmental samples include negative chemical ionisation mass spectrometry, and the use of solid phase extraction for sampling ambient air.

I. LC/MS Determination of Pesticides - Glyphosate and Phenoxy Acid Herbicides

Study Leader:	Lorna Grey, Applied Chromatography Section
Study Team:	Bick Nguyen & Paul Yang
Customer:	Environmental Monitoring and Reporting Branch (Pat Lachmaniuk), Operation Division – Pesticide Analysis Lead (John Hatton), Drinking Water Surveillance Program

Objective

To develop a high sensitivity, liquid chromatography separation, electrospray ionization mass spectrometry (LC/MS) analytical method for the analyses of glyphosate (Round Up) and chlorophenols/phenoxy acids (CP/PA) target substances, two of the most commonly used herbicides in Southern Ontario. A method for the analysis of these target substances in sample matrices such as water, vegetation, and solids with good recovery, high sensitivity, and consistency across all matrices is required to support the Pesticide Act of Ontario (PAO) and meet Ontario MOE's "Cleaner Water" and "Cleaner Ecological System" Objective.

Background

The driving forces of this project are:

1. the Operation Division (OD) of the Ontario Ministry of the Environment requires an analytical method for the analysis of glyphosate and CP/PA in various environmental matrices such as water, vegetation, and soils;

2. the Applied Chromatography Section requires an efficient method to replace the existing GC/ECD method for the analysis of CP/PA target compounds in drinking water samples (Drinking Water Surveillance Program, or DWSP).

DWSP samples are analysed by using solid phase extraction, diazomethane derivatization, and GC/ECD analysis. The current method delivers good quality data that meets ODWO and PWQO guidelines requirement but can be cumbersome because of the use of diazomethane, which is a laborious procedure. Staffing constraints dictate that this method be improved to include more efficient sample preparation and/or analysis procedure to meet increasing workload demands.

Staff of the OD require methods for the enforcement of the PAO; hence, the ability to produce consistent analytical data in various aqueous matrices, with good recoveries and superior sensitivity when operated in the presence/absence analysis mode is needed.

Results

Based on a literature search and discussions with the Glyphosate Team (Monsanto, St. Louis, KA) a new procedure has been devised for multimedia sample preparation for LC/MS analysis. Optimization of LC/MS operation parameters has been be completed by February 1999. Validation of the sample preparation procedures will been on-going and is scheduled to be completed by the end of fiscal year 1998/99.

Development of an LC/MS-based CP/PA analysis method began as a separate project and was combined with the glyphosate analysis because of the similarity of the sample preparation procedures and the operation parameters of the LC/MS instrumentation employed. An LC/MS method has been completed using CP/PA standards in addition to rodenticides, dithiopyr, MCPA, MCPB, and MCPP targets.

Current Status

Validation of sample preparation procedures for glyphosate has been parallel to method documentation. A method will be submitted to the QMO office in the 1999/2000 fiscal (April 1999) for internal audit followed by a field study with DWSP customers.

LC/MS analysis of CP/PA has been documented in method E3404 (multiresidual pesticide analysis) and will be audited by the QMO office to support OD's requirements. A similar procedure will be implemented in method E3119 in the next fiscal, audited, in order to carry out a field/equivalency study with the DWSP client.

II. Liquid Chromatography/Electrospray Ionization - Isotope Dilution Mass Spectrometry Determination of Diquat and Paraquat in Environmental Matrices

Study Leader:	Lorna Grey, Applied Chromatography Section
Study Team:	Bick Nguyen & Paul Yang
Customer:	Operation Division – Pesticide Analysis Lead (John Hatton).

Objective

To develop a high sensitivity liquid chromatography separation, electrospray ionization - isotope dilution mass spectrometry (LC/ESI-IDMS) analytical method for the analysis of paraquat and diquat herbicides in environmental samples such as water, vegetation, and solid matrices to support the Pesticide Act of Ontario (PAO) and meet Ontario MOE's "Cleaner Water" and "Cleaner Ecological System" Objectives.

Background

The Operation Division of the Ontario Ministry of the Environment requires an analytical method for the determination of diquat and paraquat herbicides in various environmental matrices. The ideal method would have the ability to produce consistent multi-media analytical data with superior recoveries, with high accuracy, and the highest sensitivity possible when operated in the presence/absence analysis mode, thereby providing an effective tool for the enforcement of the PAO. The enforcement aspect is especially important during the spraying of these herbicides, as cross-boundary pesticide drift is a common incident.

Results

Based on the original LSB method E3404, a new method has been developed for the required Data Quality Objectives (DQO) as indicated by Customers. Validation of the new method – which was based on literature methods -- along with development of a new solid phase extraction procedure that can be used for the preparation of multi-media samples, have been completed. A 2-month field study, which involved the analysis of 207 water samples, was carried out to determine sample stability, the use of preservatives, and storage conditions and times. Also included in the method is an

extensive study which validated, for the first time, that typical recoveries of native and isotopic-labelled (via deuterium) diquat and paraquat are statistically equal. This eliminated prior concerns about [H⇔D] exchanges under these sample preparation conditions and justified the use of isotopic dilution for this application.

Status

Final LSB method documentation has been on-going. The method will be submitted to the LSB Quality Management Office (QMO) and be audited by Mid-March 1999. Lorna Grey will present the results at the 31st Eastern Canada Pesticide and Environmental Contaminants Workshop, May 18, in Niagara-on-the-Lake, Ontario. The preparation of a manuscript will be done by June 1999 and submitted to the Journal of the Association of Official Analytical Chemists for publication.

III. Fast GC Determination of Dioxins, PCBs, PAHs and OC Pesticides

Study Leader:	Eric Reiner, Dioxin & Toxic Organics Section
Study Team:	Tony Chen, Rob Brunato, Karen MacPherson, Jerry Ladwig
Customer:	All Ministry Customers of Dioxin & Toxic Organics Section

Objectives

To convert methods to the Fast GC format in order to reduce analysis times and enhance instrument capacity and sample throughput.

Background

Over the past decade, methods for a number of analytes (dioxins, PCBs) have evolved towards congener specific determinations. These methods typically require longer chromatographic columns to achieve the required separations, which translates to longer analytical run times. Run times can be reduced by reducing column diameters. If the phase ratio (column phase thickness:column diameter) remains constant, the chromatographic resolution will remain relatively constant. A reduction in column diameter with constant phase ratio will give a corresponding reduction in Height

Equivalent Theoretical Plate (HETP). Therefore, shorter columns can be used to obtain the required separations *with reduced run times*. If higher temperature ramp rates (up to 120°C/min) and higher column pressures (up to 150 psi) are used, run times can be reduced even further.

Results

Methods for PCBs (congener), OC Pesticides, PAHs and Dioxins were converted to fast mode using the Hewlett Packard method translation software program (1997 version). Columns were selected to reduce analysis times as much as possible with no loss of chromatographic separation. Conditions for each of the analytes were as follows:

PCBs. The method was converted from 60 M [0.25µm, 0.25mm] DB-5 and DB-1701 columns to 20M [0.1µm, 0.1mm] DB-5 and DB-1701 columns. The analysis times were reduced from over 90 min on the 60M columns to under about 17 min on the 20M columns.

OC Pesticides. The method was converted from 30M [0.25µm, 0.25mm] DB-1 and DB-5 columns to 20M [0.18µm, 0.18mm] OC Pesticides - 1 and OC Pesticides - 2 columns. These columns were developed by Restek and are analyte-specific for OC pesticides. Analytical run times were reduced from 55 min to just over 10 min.

Dioxins. The method was converted from a 60M [0.25µm, 0.25mm] to 40M [0.18µm, 0.18mm] and 20M [0.10µm, 0.10mm] columns. Run times were reduced from 45 min to 27 and 13 min, respectively. Chromatographic separation of the most critical congener pair (1278/9-TCDD and 2378-TCDD) could not meet the 25% valley separation requirement. Future work will include a switch to hydrogen carrier gas in order to improve chromatographic separation.

PAHs. The method was converted from a 30M [0.25µm, 0.25mm] DB-5 column to 20M [0.10µm, 0.10mm] and 10M [0.10µm, 0.10mm] column. The 20M column exhibited improved chromatography, but run times were only about 30% shorter. Run times were about four times faster on the 10M column. Some critical pairs (phenanthrene/anthracene and benzo[b]fluoranthene/benzo[k]fluoranthene) can be separated, although this separation has not been fully optimized.

Current Status

Fast GC methods for congener-specific PCBs and OC pesticides have been completed and validated. Fast GC methods for Dioxins and PAH require further work to enhance the chromatographic separation. Future work includes investigating hydrogen as a carrier gas and further optimization of chromatographic parameters.

IV. SPE Cartridge Sampling and GC/MS Analysis of Aldehydes and Ketones in Ambient Air

Study Leader:	Mike Sage, Mass Spectrometry/Volatiles Section
Customer:	Standards Development Branch

Objective

To develop a SPE sampling method (GC/MS analysis) for the trace level testing of aldehydes and ketones in ambient air in support of the Standards Development Branch 3-year Standards Setting Plan. The proposed 24 hour ambient air quality criterion (AAQC) and Point of Impingement standard for formaldehyde is 65 $\mu g/m^3$. The Data Quality Objective for this study was established as 6.5 $\mu g/m^3$ i.e. 10 times lower than the proposed AAQC.

Background

Monitoring indoor, industrial, and ambient air for formaldehyde and other aldehydes is challenging because of the specificity and sensitivity needed when sampling. Currently accepted methods include US EPA TO11 and US EPA IP-6A. These methods cite the use of dinitrophenylhydrazine (DNHP)-coated, silica-based, solid phase extraction cartridges for the collection and derivatization of these analytes. The DNPH reagent reacts to form the more stable hydrazone derivative which is recovered by solvent desorption of the adsorbent bed. The sample can then be analyzed by HPLC/UV.

Recently DNPH SPE devices, using the traditional syringe barrel configuration featuring low pressure drop for high sample flow rates (up to 1.5 L/min when using a personal sampling pump) have been developed. These cartridges exhibit minimal background levels and provide sensitivity in the ppb concentration range.

A method employing GC/MS in place of HPLC/UV for the analysis of carbonyl hydrazone derivatives offers several advantages including convenience of use, reductions in solvent consumption, shorter analysis times, and mass spectra data for positive identification of analytes.

Results

A viable method for the analysis of formaldehyde in air samples collected on

LpDNPH S10 cartridges for sample concentration and formation of DNPH- carbonyl derivatives followed by gas chromatography on a HP-5MS column and mass spectrometry has been developed. The method is suitable for the analysis of formaldehyde and is sensitive enough to meet the DQO of 6.5 µg/m^3. The limit of measurement (W), limit of reliability (T) and method detection limit (MDL) were determined by following protocols described in the Laboratory Services Procedure Manual (LSB SOP 026). Formaldehyde values for W, T and MDL were 0.2, 2.0 and 0.8 µg/mL, respectively. When typical sample volumes for a 24 hour sample range from 720 - 2160 liters, the corresponding MDL value will range from 0.4 - 1.1 µg/m^3, well below the DQO.

Instrument with-in run precision for formaldehyde based on an analysis of a set of 8 standards at 2 µg/mL was < 5% relative standard deviation. Formaldehyde recovery based on a set of 8 method spikes was in the range of 75% to 110%.

Acceptable chromatography could not be achieved for aldehydes with boiling points greater than hexaldehyde. The Dowex cleanup affects the recovery of all aldehydes and ketones other than formaldehyde to varying degrees. The cleanup step is necessary to remove excess DNPH from the sample extract. Excess DNPH adversely affects chromatography.

The sample cartridge capacity for formaldehyde is 75 µg. A correlation coefficient of 0.998 was achieved for formaldehyde over a range of 0.2 to 20 µg/mL. By employing flexible sampling periods and sample flow rates the method can be applied to both AAQC and point of impingement monitoring applications for formaldehyde. The method provides several advantages compared to the currently accepted HPLC/UV method including ease of use, reduced solvent use, and shortened analysis times of ~40 minutes per analytical run.

Current Status

The method is ready for field testing evaluation in which replicate samples will be collected by using side-by-side samplers – one equipped with the new sampling cartridge, and the other with a current standard sampling method. Other carbonyl compounds (i.e. ketones) and higher boiling point aldehydes were not suitable for analysis by this method because of factors related to sample preparation and chromatography. These compounds will be evaluated by using LSB Method E3314.

V. LC/(Electrospray Ionization) MS Determination of Microcystins

Study Leader :	Steve Jenkins, Mass Spectrometry / Volatiles Section
Study Team :	Vince Taguchi
Customer :	Environmental Monitoring and Reporting Branch, Standards Development Branch

Objectives

To develop a quantitative analytical method for microcystins in drinking water by Liquid Chromatography - Electrospray Ionization Mass Spectrometry (LC-ESI/MS).

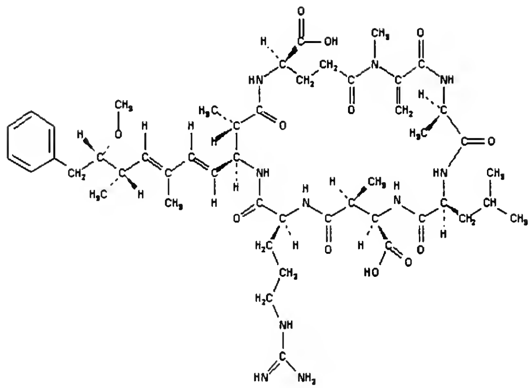
Background

Microcystins are cyclic heptapeptide hepatotoxins produced by cyanobacteria (blue-green algae; see structure below). Genera known to produce toxins include *Microcystis*, *Oscillatoria*, *Aphinizomenon*, *Anabaena* and *Nostoc*. So far, more than 50 microcystins have been identified. Microcystins have been responsible for the poisoning of fish, birds and animals in many countries. In 1996, over 40 patients undergoing dialysis treatment, in the Brazilian city of Caruaru, died from microcystin poisoning due to contaminated water. Microcystins have also been found to be tumour promoters. The most toxic and most abundant congener is microcystin-LR. The intracellular toxins are released at the later stages of the cell's life cycle or when water is treated with an algicide which lyses the cell wall. The toxicity of microcystin-LR is related to its irreversible inhibition of the protein phosphatases 1, and 2A.

Results

A procedure has been developed for the analysis of soluble microcystin-LR in drinking water. The toxin is extracted from water using a C18 Solid Phase Extraction (SPE) disk. The microcystin-LR is quantitated against the internal standard Gramicidin S (a cyclic decapeptide antibiotic). The detection limit is approximately one order of magnitude below the proposed drinking water guideline of 1.5 µg/L.

Microcystin-LR



Current Status

The present method only analyses for extracellular soluble microcystin-LR. Current plans are to investigate the analysis of other microcystins, such as -RR, -YR and -LA (those that are commercially available as standards). Development may also involve the analysis of intracellular microcystins in order to determine the toxic potential of blooms. The current method still requires an improvement in precision and accuracy. This is limited by the unavailability of instrument automation and a suitable concentrator.

The microcystin-LR is mass analysed at low resolution (1000 RP) on a tandem hybrid mass spectrometer to make the method transferable to low resolution (quadrupole or ion trap) mass spectrometers. This increases the possibility of detecting interferences. No interferences have been detected so far in the limited number of samples analysed. High resolution mass spectrometry may be utilised if found to be necessary.

VI. Negative Ion Chemical Ionization (NICI)/MS Determination of Toxaphenes and Other Halogenated Organics

Study Leader :	Vince Taguchi, Mass Spectrometry/Volatiles Section
Study Team :	Rocsana Lega
Customer :	Environmental Monitoring and Reporting Branch (Surface Water Section, Biomonitoring Section)

Objectives

1. To implement a screening technique for halogenated organics using Dissociative Electron Attachment (DEA) NICI. This technique will supplement the information obtained by the characterization of extractable organics (LSB Method EXT3186).

2. To develop an Electron Capture Negative Ion Mass Spectrometry (ECNIMS) characterization analysis for toxaphenes and other halogenated organics.

Background

Extractable organics are identified by GC-MS technology (EXT3186) using electron ionization (EI). This technology can be used to identify a broad range of organics. However, halogenated organics present at low concentrations detectable by GC-ECD may not be detectable by GC-(EI)MS.

NICI can be used to reach detection limits comparable to GC-ECD and also provide mass spectrometric information. ECNIMS utilizes thermal (low energy) electrons which are captured by a compound having an electron affinity. At low ion source temperatures, less fragmentation occurs than at higher ion source temperatures. The abundances of higher mass ions are correspondingly higher at lower source temperatures. DEA is an NICI technique in which the ion source is kept at a high temperature (350°C) to dissociate Cl^- from chlorinated organics (detectable at m/z 35/37) and Br^- from brominated organics (detectable at m/z 79/81). By monitoring only these ions, it should be possible to obtain the retention times of the halogenated organics in the presence of electron capturing organics that are not halogenated. These compounds can be further analyzed by a low temperature NICI technique (ECNIMS) for identification.

ECNIMS can be optimized for high mass ions by keeping the ion source temperature in the range of 100-120°C. The standard EI/CI source on the VG Trio-2 single quadrupole mass spectrometer is capable of regulating at 150-170°C with the filament on continuously. A dedicated CI source capable of regulating at 100-120°C was obtained to optimize the ECNIMS analyses. This source will be used to identify/confirm toxaphene congeners and other halogenated organics.

Results

The DEA technique was set up on a standard VG Trio-2 EI/CI source with the following modifications: the movable ion exit was replaced by a fixed ion exit plate with a CI aperture; the opening in the solid probe seat was plugged with a part from a VG ZAB-EQ source; and the source was set to 350°C, the highest temperature permitted with the existing power supply and heating element.

DEA was applied to some sediment extracts from the St. Clair River. These extracts had previously been analyzed by GC-(EI)MS on a GC-MSD. DEA was extremely useful in locating the chlorinated and brominated compounds. From these retention times, the corresponding ECNIMS spectra were examined.

The dedicated CI source was installed and tested. The lowest temperature at which the source would regulate with the filament on continuously was 105°C. With methane or 2% ammonia/methane as reagent gases, the source became contaminated rapidly. This source has an ion volume that is 1/10th that of the standard source. As such, it has no repeller and ions must be expelled from the ion volume using the ion extraction lens. In addition, impurities (higher hydrocarbons) in the reagent gas can cause rapid contamination. This problem was solved by switching to ammonia as the reagent gas.

ECNIMS spectra of the sediment samples were obtained at a source temperature of 110°C. The EI data showed a number of PCBs (tetrachloro- to heptachloro-) as well as pentachlorobenzene, hexachlorobenzene, heptachlorostyrene, octachlorostyrene, and octachloronaphthalene. The ECNIMS data showed more heptachloro-PCBs as well as several octachloro-, a nonachloro- and decachlorobiphenyl. In addition, two hexachlorostyrenes, a heptachloronaphthalene, and a tribromotoluene were detected.

ECNIMS was applied to Toxaphene Mix 1 from Dr. Ehrenstorfer reference materials. This is a mixture of toxaphene congeners designated as Parlar Numbers 26, 32, 50, 62 and 69. Compounds represented by Parlar No's 26, 50 and 62 can account for up to 50% of the toxicity in fish. Detection limits using the dedicated CI source were

approximately a factor of 5-10 times lower than those obtained with the standard EI/CI source.

Current Status

Typical and ultimate detection limits using SIM and ECNIMS at 110°C are presently being determined. Typical detection limits appear to be in the range of 2-10 pg for Parlar 26, 32 and 50. Detection limits for Parlar 62 and 69 are higher. Fish extracts previously analyzed by GC-ECD will be re-analyzed using ECNIMS.

VII. LC-MS/MS Method for Nonylphenol Ethoxylates

Study Leader :	Patrick Crozier and V.Y. Taguchi, Mass Spectrometry/Volatiles Section
Study Team :	J.B. Plomley (MDS Sciex)
Customer :	Ian Smith, Water Policy Branch; R. Kettry, Canada Ontario Agreement (COA), STP Characterization

Objectives

To develop a selective and sensitive analytical method for the testing of nonylphenol ethoxylates (NPEs) that are not amenable to analysis by GC-MS; to use an LC-MS/MS method to test sewage treatment plant (STP) samples for the presence of NPEs in order to delineate the extent of NPE contamination in wastewater. The new method will complement the existing LSB GC-MS method for the characterization of extractable organics.

Background

Nonylphenol ethoxylates (NPEs) of the form 4-$(C_9H_{19})C_6H_4(OCH_2CH_2)_nOH$, where n = 1-16, are of environmental concern because of their tendency to degrade to 4-nonylphenol, a member of a group of chemicals known as endocrine disruptors. NPEs themselves have been shown to be weakly estrogenic. NPEs are non-ionic surfactants utilized in domestic and industrial cleaners as well as in the textile and pulp and paper industries. As they are a component of various cleaners, NPEs have been detected in various wastewater streams and in sewage treatment plants (STP). In

1990, over 4 kton of NPEs were used in Canada alone.

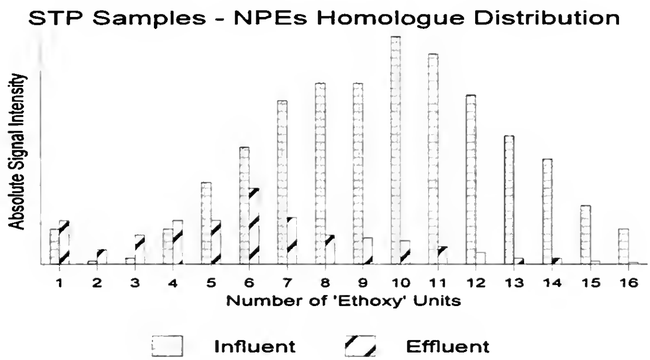
Despite the growing concern with regard to NPEs, very few selective and sensitive analytical techniques exist for their detection in complex matrices such as STP influents, sludges and effluents. A requirement for low detection limits and compound specificity coupled with the high chemical backgrounds in complex matrices preclude the use of GC-FID, LC-UV or LC-Fluorescence as detection tools. Some NPEs can be analyzed by GC-MS, but GC-MS techniques are biased towards the lower molecular weight NPE homologues due to the poor volatility of higher molecular weight NPEs. The absence of higher molecular weight NPEs (> $(EtO)_6$) in GC-MS analyses is a limitation of the technique. The limitation of GC-MS can be circumvented by the use of LC techniques. Most LC-MS applications of surfactant analysis have been biased towards the chromatographic resolution of linear/branched alcohol ethoxylates or alkyl sulphates, which separate based upon aliphatic chain length on reversed phase systems. Under such reversed phase conditions, NPE homologues present in the mixture remain unresolved, such that the ethoxylate distribution must be derived from the extracted ion chromatogram of each molecular ion. In the absence of chromatographic separation from matrix species, utilization of only a single stage of MS can result in the adulteration of ethoxylates profiling due to the presence of isobaric interferences. Consequently, a tandem mass spectrometric (MS/MS) technique which offers an inherent degree of selectivity (via precursor ion isolation) and specificity (precursor ion fragmentation to form a product ion spectrum fingerprint) was explored as a means of eliminating matrix interferences while maintaining compound selectivity and eliminating the need for chromatographic separation.

Environmental monitoring of NPEs would be facilitated by a rapid flow injection (FI)-MS/MS screening technique that would give a presence/absence of total NPEs above/below a specified objective or guideline. Presence above the objective/guideline would result in further speciation of the NPEs by LC-MS/MS. This approach would obviate the need for speciation of samples containing no NPEs or containing NPEs below the objective/guideline.

Results

A rapid screening technique for the detection of nonylphenol ethoxylates (NPEs) was developed using flow injection analysis (FIA) combined with atmospheric pressure ionization (API) and mass analysis by precursor ion scanning and multiple reaction monitoring (MRM) on a triple quadrupole mass spectrometer. The mass spectra of NPE mixtures by electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI), in the presence of 70:30 methanol:water (1% acetic acid), were characterized by protonated molecular ions separated by 44 μ, corresponding to a homologous series of ethoxylates units. MS/MS analysis of each homologue revealed

a common product ion at *m/z* 133 for 4-16 ethoxy units (EtO_4 - EtO_{16}). Consequently, precursor ion scanning was used as a means of profiling NPEs while retaining homologue selectivity and obviating chromatographic separation. FIA at 200 µL/min allowed analysis times < 60 seconds which is conducive to a high throughput screening technique. In the same experiment, MRM of a transition other than that leading to *m/z* 133 was performed for all precursor ions ranging from EtO_1 - EtO_{16}. This allowed the detection of EtO_1 - EtO_3 and provided a confirmatory technique for EtO_4 - EtO_{16}. The precursor ion scans and MRM scans were combined in one experiment providing a quick semi-quantitative analytical tool. Based on the wet chemical preparation scheme and MS/MS instrument detection limits, sample screening down to ~ 50 ng/L total NPEs can be achieved. Representative sewage treatment plant (STP) influent and effluent samples were successfully profiled using the FI-MS/MS analytical method. Cursory results, based on a single STP site, indicated that, although effective at reducing NPEs from the waste stream, the treatment process does not completely eliminate NPEs (see figure).



Current Status

Sewage treatment plant (STP) samples, which were submitted and characterized by GC-MS for extractable organics, have been prepared and are ready to be analysed by LC-MS/MS. Samples were selected to cover several STP locations, assorted sample types (influent, effluent, sludge, etc..) and 'ng/L to mg/L' concentrations of NPEs (as determined by GC-MS). Reversed phase and normal phase chromatographic separations of NPEs have been developed and when combined with the existing precursor ion scanning/MRM MS detection method should give quantitative data to establish the presence/absence and levels of NPEs in Ontario sewage treatment plants.

Publications and Presentations

1. Jeffry B. Plomley and Patrick W. Crozier. Rapid Screening of Nonylphenol Ethoxylates in Wastewater by Combined Precursor Ion Scanning and MRM. Proceedings of the 46th ASMS Conference on Mass Spectrometry and Allied Topics, Orlando, Florida, May 31 - June 4, 1998; p. 369

2. Jeffry B. Plomley and Patrick W. Crozier. The Characterization of Nonylphenol Ethoxylates in Sewage Treatment Plants by Combined Precursor Ion Scanning and MRM. The 15th (Montreux) Symposium on Liquid Chromatography - Mass Spectrometry (LC/MS), Montreux, Switzerland, November 9 -10 ,1998.

3. Jeffry B. Plomley, Patrick W. Crozier and Vince Y. Taguchi. The Characterization of Nonylphenol Ethoxylates in Sewage Treatment Plants by Combined Precursor Ion Scanning and MRM. Journal of Chromatography A, in press, 1999.

VIII. Flow-Through Microwave Digestion of Soil Samples for Metals

Study Leader :	Jane Thrush, Physical Chemistry and Litigation Services
Customer :	Standards Development Branch (Phytotoxicology Section)

Objectives

To reduce sample preparation time, improve throughput, reduce the use of concentrated acids for sample extraction, and to reduce sample handling by staff. There is a potential for increased automation; if the method works, the current extraction used for LSB Method E3073A can be changed to this extraction procedure.

Background

Microwave digestion has become more prevalent and several studies show that sample preparation time is reduced by using this technology. The "flow- through" microwave system is an important development in the technology as a larger number of samples can be processed unattended than through a "batch" system. All quality

control and test samples are handled in a consistent manner by computer, thereby maintaining reproducibility while reducing staff time. Questron Canada in cooperation with MOE (former Research Advisory Committee grant) developed a computerized extraction system based on microwave technology.

Results

The operation of the equipment using varying conditions of acid concentration, temperature, pressure and time have been studied. Conditions were found that gave extraction recoveries comparable to that of the existing method using an in-house reference soil material. Results are shown in the Table below:

Comparison of Routine and Microwave Extraction Using In-House Control RS92 Soil Sample (µg/gram dry weight)

PARAMETER	Standard Extraction Technique	Microwave Technique
Molybdenum	0.06	nd**
Strontium	30	36
Aluminum	11000	13000
Copper	8.3	26
Calcium	21000	22000
Beryllium	0.39	0.39
Vanadium	35	36
Magnesium	6100	6200
Chromium	14	17
Iron	16000	14000
Manganese	270	290
Nickel	7.2	7.7
Cobalt	4.3	4.4

Cadmium	0.42	0.39
Lead	16	13
Zinc	47	56
Barium	37	53
Boron	8	8.5

**nd = not detected

Current Status

As is demonstrated by the results above, excellent agreement was obtained between metal concentrations extracted by the flow-through microwave procedure compared to conventional acid digestion. More work needs to be done to fine-tune the extraction parameters of acid concentration, temperature, pressure and time to establish the best conditions for the most efficient extraction.

B. Methods Development

Introduction

Work continued during the past year to improve the speciation of PCBs in various sample types. PCBs present an interesting challenge, because much of the existing environmental PCB contamination in years past resulted from the use of industrial mixtures of PCBs called Aroclors. The quantitation of PCBs only in groups was not acceptable for all applications, because there is a considerable difference in toxicity between individual PCB congeners. Therefore, although we still need good methods to differentiate between the various Aroclor patterns, new methods are needed that are able to accurately quantify those individual PCBs that have greater toxicity. In addition, "weathering" over a number of years has in some cases changed the original Aroclor pattern sufficiently that individual congener analysis is now necessary for accurate quantitation.

One of the most difficult applications in recent years has been the development of a method for Total Petroleum Hydrocarbons (TPH) in water samples. Because TPH consists of such a wide range of hydrocarbon compounds, the method requires a determination of both volatile and semi-volatile components by using different techniques. The work reported here is part of a national effort to harmonize TPH methodology, let by the Canadian Council of Ministers of the Environment (CCME). In other research this year, the work on developing a new method for taste and odour compounds in water was continued, and a new method for nitriloacetic acid in water was developed. Finally, a semi-quantitative method was developed for metals in environmental samples.

I. Large Volume Water Method for Aroclors and PCB Congeners

Study Leader:	Stephanie Lemanik, Applied Chromatography Section
Study Team:	Mary Wilson, Marilyn Pitcher, Paul Yang
Customer:	Environmental Monitoring and Reporting Branch (D.Boyd)

Objectives

To develop an analytical method for the analysis of polychlorinated biphenyl (PCB) congeners and Aroclors using large volume ambient water samples (16-litre), solid phase extraction, and GC/MS analysis at sub-ppt (part-per-trillon) detection limits to meet Ontario MOE's "Cleaner Water" Objective.

Background

The Laboratory Services Branch of the Ontario Ministry of the Environment has been analyzing water samples for PCB congeners, including dioxin-like PCBs, and Aroclors using various analytical techniques at high ppt and/or low ppb (part-per-billion) concentrations. The Great Lakes Monitoring and Assessment program (EMRB) required a new and more sensitive method for the analysis of these environmental pollutants at low ppt concentrations.

Results

Working with the customer, data quality objectives (DQOs) have been decided for the target compounds (PCB congeners), which include detection limits and data reporting format. Consensus on the selection criteria for a group of 46 PCB congeners to be monitored has been done. In order to achieve low ppt detection limits, two sample preparation procedures that allow the concentration of a 1-L and 16-L ambient water samples into a 50-μL and 1-mL final volumes, respectively, and the analysis of the PCB congeners and dioxin-like PCBs using a bench top mass spectrometer were investigated. Quality control and quality assurance (QC&QA) protocols have been enhanced by using a total of 13 deuterated internal standards representing PCB, polycyclic aromatic hydrocarbon (PAH), and organochlorine (OC) compound classes. Field studies were completed, which included a comparison between liquid/liquid and solid phase extraction techniques by using TJ Baker Speedisks.

Current Status

Depending on the DQOs needed for a specific investigation, either liquid/liquid microextraction or solid phase extraction using TJ Baker Speedisks can be used to deliver high performance analytical data. The liquid/liquid microextraction procedure outperforms the solid phase extraction method with respect to analyte recoveries, but gives higher detection limits because of the inherent limitation imposed by the use of a 1-L ambient water sample. The following PCB concentration data can all be determined by using this method:

1. individual concentrations of 46 PCB congeners;

2. total concentration of each of the 10 PCB congener groups (mono– to deca–PCB);

3. total concentrations of Aroclors 1242, 1254, and 1260.

Preparation of the documentation required for a final LSB method has been on-going. The method will be submitted to the LSB Quality Management Office and be audited by the Section QA coordinator before the end of March 1999. The addition of PAH and OC target analytes to the method will be investigated in 1999, along with the laboratory and field validation of sampling protocols using the on-site solid phase extraction techniques.

II. Method for Dioxin-like PCBs in Environmental Samples

Study Leader:	K. MacPherson, Dioxins & Toxic Organics Section
Study Team:	T.Kolic, V.Khurana
Customer:	Environmental Monitoring and Reporting Branch (Fish Contaminants & Surface Water)

Objectives

To develop an isotope dilution method for the determination of congener specific PCBs. The World Health Organization (WHO) has assigned toxic equivalent factors (TEFs) for 12 of the 209 possible PCB congeners. These compounds were assigned TEFs due to their demonstrated "dioxin-like" toxicological effects. These 12 congeners

are collectively referred to as dioxin-like PCBs (DLPCBs).

Background

PCBs were used world wide from the 1930 to the early 1970s as dielectric fluids, and as chemical additives to paints, inks, sealants and numerous other materials. A number of different technical mixtures (Aroclors) based on % chlorine content were manufactured. Significant concentrations of these mixtures have found their way into the environment due to poor handling practices. After a number of years in the environment, the composition of these mixture are no longer representative of the original mixture due to weathering. There are 209 possible PCB congeners of which about 130 are typically found in Aroclor mixtures. Of these 130, 12 behave like 2,3,7,8-TCDD in biological organisms (bind to AH receptor) and have been identified as dioxin-like PCBs (DLPCBs). The concentrations of these 12 congeners in environmental samples are lower than the concentrations of many of the other congeners and therefore to identify and quantify them, a congener-specific isotope dilution HRMS method similar to that used for dioxins and furans is required. Determination of TEQ values for the PCB component of the sample is a more accurate representation of the toxicity of the sample, especially for one that has undergone considerable weathering.

Results

The list of DLPCBs includes 4 coplanar (BZ#: 77, 81, 126, 169) and 8 mono-ortho congeners (BZ#:105, 114, 118, 123, 156, 157, 167 and 189). The coplanar congeners were isolated with the dioxins and furans in a classical 3 column (silica/alumina/carbon) dioxin/furan method. The mono-ortho congeners elute before the dioxins and furans on the second (alumina) column. The method was developed to force polychlorinated diphenyl ethers (PCDPEs) into the mono-ortho PCB fraction, away from the dioxin/furan fraction. PCDPEs interfere with polychlorinated dibenzofurans giving rise to biased high quantitative results for the furans, therefore a single fraction dioxin/furan/PCB method was not pursued.

Current Status

The method is complete for biota samples. Method Detection Limits have been determined and are summarized in the table below. Future work planned involves modification of the method for other sample types including soils & sediments, air, vegetation, and water. Fast GC with parallel column (2 columns, simultaneous injection) analysis will be investigated.

Method Detection Limits (MDLs)**
for DLPCBs in Fish

IUPAC I.D.	MDL(PPT)
PCB 81	2.0
PCB 77	2.9
PCB 123	3.3
PCB 118	61
PCB 114	3.1
PCB 105	22
PCB 126	2.5
PCB 167	1.9
PCB 156	6.0
PCB 157	2.9
PCB 169	1.8
PCB 189	1.0

**MDLs determined with 10 replicate Alaskan Polock fillets, 9 degrees of freedom.

III. Congener-Specific Method for PCBs in Soil, Sediment, and Biota

Study Leader:	Rob Brunato, Dioxins & Toxic Organics Section
Study Team:	Eric Reiner, Tony Chen
Customer:	Emvironmental Monitoring and Reporting Branch (Fish Contaminants, Surface Water), Standards Development Branch (Phytotoxicology, Aquatic Toxicology) and Region Operations Division

Objective

To develop a new analytical method to improve the non congener-specific analysis of low level PCB congener groups in soil, sediment, and biota – and to reduce analysis time.

Background

PCBs were used in electrical transformers, caulking, paints, inks, insecticides and dielectric fluids. The use of PCBs has been banned since the late 1970s. Technical mixtures of PCBs, called Aroclors, have distinct congener patterns that are dependent on the degree of chlorination. Through the years, Aroclors in environmental samples have become aged or weathered and the PCB patterns observed in these samples are no longer representative of the patterns in the original Aroclor mixtures. Congener-specific data gives a more accurate indication of the state, toxicity and levels of PCBs in the sample and environment.

Tradionally PCBs are identified as total Aroclor mixtures. Although this approach is good for non weathered samples, it lacks certain desirable features. For instance, the identification of specific congeners is not possible with the conventional (total PCB) method. It is possible, by using a congener-specific method, to identify which PCB congeners are present in a sample, thus giving a more accurate evaluation of the sample's toxicity.

Results

A Fast GC congener-specific method has been developed for the analysis of PCBs in environmental samples. This technique uses a thin film, short narrow bore column. A Hewlett Packard 6890 GC was used with dual injectors and dual micro EC detectors. The columns used were a 20m DB-5 [0.1 mm ID and 0.1 µm film thickness] and a 20m DB-1701 [0.1 mm ID and 0.1 µm film thickness]. Injector temperature was 250°C and both ECDs were maintained at at 300°C. Helium was used as carrier gas at a rate of 0.4 mL/min. The initial oven temperature was 90°C, it was initially ramped to 160°C at 35.5°C/min., with a hold time of 0.28 minute. It was then ramped to 200°C at 71°C/min. and held for 6.7 minutes. The column head pressure was 70 psi.

The fast GC method was shown to be reproducible and rugged. Fast GC results were comparable or better than those of the conventional GC method. Run times were reduced by approximately 75%, going from 84 minutes with the conventional method to 20 minutes with the Fast GC method. Data from spiked matrix samples resulted in MDL values of 1-3 ng/g for the majority of the congeners analyzed, which shows that PCBs can be analyzed using Fast GC/ECD for environmental samples.

Certified reference materials have been analyzed. Results are in good agreement with target values for most congeners (see tables 2 and 3).

The 56 target PCB congeners to be analyzed, shown in Table 1, were chosen based on their environmental occurrence, abundance, and toxicity.

Table1: PCB Congener #'s to be Analyzed

Trichlorobiphenyls:	18,19,22,28,33,37
Tetrachlorobiphenyls:	44,49,52,54,70,74,77,81
Pentachlorobiphenyls:	87,95,99,101,104,105,110,114,118,119,123,126
Hexachlorobiphenyls:	128,138,149,151,153,155,156,157,158,167,168,169
Heptachlorobiphenyls:	170,171,177,178,180,183,187,188,189,191
Octachlorobiphenyls:	194,199,201,202,205
Nonachlorobiphenyls:	206,208
Decachlorobiphenyls:	209

Table 2: Results from Analysis of PCB Congeners in Reference Sediment EC3

PCB Congener # (from table 1)	Expected Value (ng/g ± std. dev.)	# of Analyses	Average Result (ng/g ± std. dev.)
18	9.0 ± 4.7	8	9.2 ± 1.7
28	19 ± 8.6	8	15 ± 1.2
44	33 ± 15	8	44 ± 7.9
52	36 ± 13	8	29 ± 1.8
87	17 ± 3.7	8	64** ± 3.5
101	39 ± 7.2	8	33 ± 3.1
105	13 ± 4.3	8	19 ± 3.1
110	53 ± 21	8	36 ± 1.9
118	29 ± 5.4	8	29 ± 3.1
128	7.3 ± 3.2	8	6.4 ± 0.5
138	25 ± 6.3	8	26 ± 2.0
151	8.1 ± 4.1	8	9.1 ± 0.7
153	24 ± 4.1	8	23 ± 2.0
170	8.9 ± 1.3	8	9.6 ± 0.8
180	15 ± 6.6	8	14 ± 1.2
183	4.9 ± 1.8	8	3.9 ± 1.2
194	5.2 ± 2.1	8	4.7 ± 0.7
201	8.3 ± 2.4	8	7.2 ± 0.6
206	5.2 ± 2.1	8	4.0 ± 0.6
209	19 ± 11	8	15 ± 1.5

** concentration of PCB #87 is over-estimated due to overlap from DDE interfering peak

Table 3: Analysis of PCB Congener Reference Fish Carp-1

PCB Congener (# from table 1)	Expected Value (ng/g)	# of Analyses	Average Result (ng/g)
52	124 ± 32	3	140
101/90	124 ± 37	3	130
105	54 ± 24	3	51
118	132 ± 60	3	130
138/163/164	102 ± 23	3	100
153	83 ± 39	3	96
170/190	22 ± 8	3	22
180	46 ± 14	3	48
187/182	36 ± 16	3	39

All Biota samples were prepared using LSB method E3136A (The Determination of PCBs, OCs and CBs in Fish, Clams and Mussels by GC/ECD). All sediment samples were prepared using method E3270A (The Determination of PCBs, OCs and CBs in Soil and Sediments by GC/ECD).

As can be seen from tables 2 and 3, the PCB results generated by using the new method are in excellent agreement with the values as reported for the certified reference materials tested. In table 2, the average percent standard deviation is three times lower than was reported for the reference material, which shows that the precision of the new method is excellent.

Current Status

Method development is complete. The method (LSB METHOD E3411A) is being used to routinely analyze samples. Subject to an LSB internal audit, the method as described is expected to achieve the "routine approved" status by the end of FY 98/99.

IV. Method for Taste and Odour Compounds in Water Using Ambersorb 572 and High Resolution MS

Study Leader:	J-P.F.P. Palmentier, Mass Spectrometry/Volatiles Section
Study Team:	Vince Taguchi
Customer:	DWSP and drinking water customers (including Metro Works); MOE Regional Offices; County Regional Laboratories

Objective

To develop a general GC-HRMS method for taste and odour causing compounds by modifying the existing method for geosmin and 2-methylisoborneol (2-MIB) to incorporate 4 additional compounds: 2,3,6-trichloroanisole, 2,4,6-trichloroanisole, 2-isopropyl-3-methoxypyrazine and 2-isobutyl-3-methoxypyrazine.

Background

Taste and odour problems occur seasonally in drinking and surface waters around North America. Six compounds have been identified as being responsible for imparting earthy, musty taste and odour qualities to water, food and soil. These include geosmin, 2-methylisoborneol (2-MIB), 2,3,6-trichloroanisole (TCA), 2,4,6-TCA, 2-isopropyl-3-methoxypyrazine (IPMP) and 2-isobutyl-3-methoxypyrazine (IBMP). Geosmin and 2-MIB are semi-volatile metabolites of actinomycetes and blue-green algae and are most often responsible for taste and odour events. IPMP is another taste and odour causing compound resulting from actinomycetes activity in water and soil. IBMP has been found in food; 2,3,6-TCA and 2,4,6-TCA are formed from reactions occurring during chlorination of drinking water or are discharged in Kraft pulp mill effluent. Human threshold odour concentrations for these six compounds have been reported as 10 ng/L for geosmin, 29 ng/L for 2-MIB, 7-30 ng/L for 2,3,6-TCA, 2-5 ng/L for 2,4,6-TCA and 2 ng/L for both IPMP and IBMP. By modifying the LSB Ambersorb 572/GC-HRMS method for geosmin and 2-methylisoborneol (2-MIB) to incorporate the additional 4 compounds, a general method for taste and odour compounds would be available. The new method would retain the high productivity and rapid (<48 hr) turnaround times of the former method.

Results

Previous work demonstrated the feasibility of separating all of the analytes with a modified temperature program on the existing Rtx-1701 column. The isotopically-labelled standard, d_5-2,4,6-TCA, was purchased for the quantitation of 2,3,6-TCA and 2,4,6-TCA by isotope dilution. 2-Methoxypyrazine (2-MP) was found to be unsuitable as an internal standard because of its poor chromatographic properties. Availability of an isotopically-labelled methoxypyrazine was investigated.

CDN Isotopes in Quebec indicated that they were unable to synthesize labelled IPMP and/or IBMP. Custom-synthesized deuterated standards were available at a cost of $10,000 (US) each. The standards, 2-ethyl-3-methoxypyrazine and 2-sec-butyl-3-methoxypyrazine were investigated as possible internal standards. Both compounds were found to have retention times suitable for the analysis. Ambersorb 572 recovery experiments using high purity water and spiked matrix samples showed good recoveries for both compounds.

This work was presented by J-P. Palmentier at the EnviroAnalysis '98 conference in Ottawa. The paper was entitled "The Determination of Taste and Odour Compounds in Water using Ambersorb 572 and High Resolution Mass Spectrometry" and was co-authored by Vince Taguchi.

The molecular ion of d_5-2,4,6-TCA was initially chosen to monitor the internal standard for 2,3,6-TCA and 2,4,6-TCA. However, it was discovered that the ^{13}C and ^{15}N isotope peaks for a fragment of PFTBA interfered with the molecular ion. The resolving power (RP) required to separate these interferences from the d_5-2,4,6-TCA were calculated to be 9,874 and 13,938, respectively. Because the analysis had been set up for 7,000 RP, the M-15 fragment was chosen for the quantitation. The method was tested on spiked high purity water samples and on spiked samples to check for matrix effects. No interferences were observed.

A potential interference in the geosmin analysis was discovered. This interference was resolved from geosmin at m/z 112.0888 on a Restek Rtx-1701 column or on a new 30m DB-1701 column. When the column was shortened due to deterioration of the chromatography, the interference began to co-elute with geosmin. To resolve the 2 compounds, the temperature program was lengthened in one segment. This lengthened the analysis time by approximately 25%. This problem demonstrates that all "1701" GC columns are not equivalent. The Rtx column can be shortened considerably and run for longer periods without replacement or lengthening of the GC temperature program.

Current Status

Performance data for the method validation are presently being obtained. 2-sec-butyl-3-methoxypyrazine has been selected as internal standard for 2-IPMP and 2-IBMP because it is in the same experiment function as the target analytes. The method should be completed by the end of FY 98/99.

Publications and Presentations

Palmentier, J-P. F.P., Taguchi, V.Y., Jenkins, S.W.D., Wang, D.T., Ngo, K-P and Robinson, D. "The Determination of Geosmin and 2-Methylisoborneol in Water using Isotope Dilution High Resolution Mass Spectrometry. Wat. Res. Vol. 32, No. 2 287-294."

EnviroAnalysis '98: Proceedings of the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment. May 11-14, 1998 Ottawa, Ontario, CANADA. "The Determination of Taste and Odour Compounds in Water using Ambersorb 572 and High Resolution Mass Spectrometry. J-P. F.P. Palmentier and Vince Y. Taguchi, p 123-127".

V. Semi-Quantitative Method for Characterization of Metals in Environmental Samples Using ICP-MS

Study Leader :	Mark Powell
Customer :	Environmental Monitoring and Reporting Branch (Partners in Air Program)

Objectives

To develop a technique for the characterization of environmental matrices for trace metal analysis. This technique will be used as a tool for analytical method development and target analyte identification in screening procedures. It is needed to provide semi-quantitative results to high schools for samples submitted under the Partners in Air program.

Background

An important part of any analytical method development for trace metal analysis is the characterization of the matrix which contains the target analytes. To know what is in a matrix gives the analyst a better idea of what may bias the target analyte in terms chemical and spectroscopic interferences. By understanding these potential effects, the analyst can make decisions regarding the design of the method and choice of analytical technique.

ICP-MS can be used to characterize a matrix by scanning elements of the periodic table to give a semi-quantitative response in terms of io*ns per atomic mass unit produced*. The spectrum will give the isotope ratios of target analytes as well as an indication of the major, minor and trace concentrations of elements in the sample. The spectrum can then be examined for interferences on target analytes.

Another application for the ICP-MS semi-quantitative method is analyte identification. Isotope ratio analysis is absolute in the identification of an element (excluding mono-isotopic elements). By using this technique, absolute confirmation of element presence in a sample is possible. This application can be very useful for court case samples or emergency samples.

In addition, this technique can be used for rapid screening in applications where quantitative analysis is needed and a very high number of samples are submitted. The semi-quantitative scan can be applied to samples prior to quantitative analysis to have a presence/absence confirmed. If the analyte is absent, the quantitative test will not need to be done.

Results

Preliminary work with the Varian Ultramass and the Sciex Elan 5000 show promising results. A procedure has been developed to scan elements of the periodic table and define isotope ratios. An application for characterization has been conducted on a fish tissue matrix in order to determine which analytical technique would be appropriate for a quantitative analytical method. Figures A through D (next page) show the mass spectra from a digest of a walleye from Moira Lake in Central Ontario. As can be seen, majors, minors and trace elements are represented by isotopes of the element forming at each relative atomic mass unit. These mass spectra can be examined for levels of target analytes and potential interferences.

Current Status

Work will continue in this area to develop a documented semi-quantitative method with a LIMS series number to use this technique for various environmental applications, some of which were mentioned above. The characterization of fish tissue will be used to develop a quantitative ICP method to replace the existing atomic absorption technique and is expected to be on-line by June 1999. The method is currently being used for the semi-quantitative determination of metals in lo-vol air filters and moss bags submitted under the Partners in Air program.

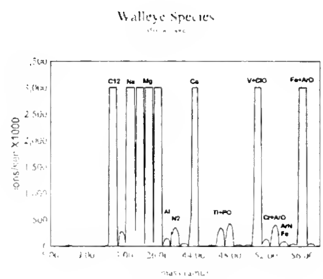


Figure A

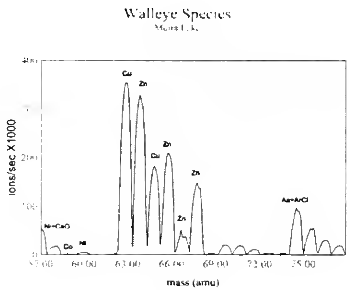


Figure B

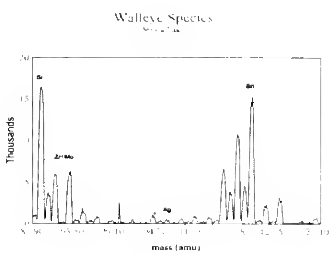


Figure C

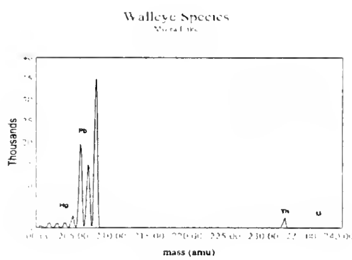


Figure D

VI. Method for Nitriloacetic Acid in Water

Study Leader :	Bernie Wright, General Chemistry & Microbiology Section
Customer :	Environmental Monitoring and Reporting Branch (P. Lachmaniuk)

Objectives

To develop an Ion Chromatographic method for the analysis of Nitrilotriacetic Acid in drinking water, with a detection limit of 0.1 mg/L as NTA.

Background

Nitrilotriacetic Acid (NTA) is widely used as a replacement detergent builder in order to reduce phosphate discharges in sewage effluents. Eutrophication problems associated with phosphorous discharges entering surface waters are reduced with NTA. NTA is also a suspected CLASS 1 carcinogen and a strong chelating agent. The effect of this compound on the distribution of metals within the aquatic ecosystem and the possible human effect from potable and ground water consumption make it an environmental concern. The maximum acceptable concentration for NTA in drinking water is 0.3 mg/L, established by the Ontario Ministry of Environment (Ontario Drinking Water Objectives - Revised 1994).

Results

A method for the Determination of Nitrilotriacetic Acid in drinking water has been developed. Modification of a Dionex 4000i (gradient elution of sample) in conjunction with a Dionex DX-100 system, 2 AG11 and 1 As11 columns are used to resolve the NTA peak. The operating range of the system is 1.0 mg/L NTA with a detection limit of 0.01 mg/L as NTA.

Current Status

The NTA method has been submitted to the Quality Management Unit and approved for use. The method has been on-line since June, 1998.

VII. Method for Total Petroleum Hydrocarbons (TPH) in Water

Study Leader:	Dave Morse
Customer:	Standards Development Branch

Objectives

To provide the Branch with the capability to analyze water for potential petroleum contamination, providing both quantitation and product identification.

Background

Petroleum hydrocarbon analysis has been performed by numerous techniques, primarily for the decommissioning of contaminated sites with potable groundwater. The Laboratory Services Branch, in support of the recently published MOE document "Guidance on Sampling and Analytical Methods for Use at Contaminated Sites" is in the final stages of development for a technique which rapidly screens for Petroleum Hydrocarbons using a combination of headspace gas chromatography and liquid/liquid solvent extraction, followed by a combination of gas chromatography and gravimetric analysis.

Also, the Laboratory Services Branch is in the final stages of development for a similar technique which will allow the identification of the type of petroleum contamination over an extended defined carbon range, C5 to C50, primarily for spill situations. This technique also uses a combination of headspace gas chromatography and liquid/liquid solvent extraction, but is followed by high temperature gas chromatography.

Results

1. <u>Determination of Petroleum Hydrocarbon in Water for the Decommissioning of Contaminated Sites</u>.

This technique is divided into two groups, Light, C5 to C24, and Heavy, approximately C17 and greater. The Light group is further divided into total purgeables, C5 to C10, and extractables, C10+ to C24. Total purgeables are analyzed by headspace gas chromatography, extractables are analyzed by liquid/liquid extraction

with hexane followed by silica separation and gas chromatography. The Light group recovery is approximately 80%, with a method detection limit of approximately 0.10 mg/L (ppm). The Heavy group is extracted by the same technique as the extractable portion of the Light group but is quantitated by gravimetric analysis. The recovery for the Heavy group is approximately 80% with a method detection limit of 1 mg/L (ppm).

2. Determination of Total Petroleum Hydrocarbon (C5 to C50) in Water.

For this method, total petroleum hydrocarbon (TPH) is defined as all petroleum hydrocarbons from n-pentane, C5 to n-pentacontane, C50. This hydrocarbon range is divided into three distillate ranges; light, C5 to C10 (ie. gasoline, naphtha), medium, C10 to C24 (ie. diesel, jet, home heating fuel) and heavy, C24 to C50 (ie. lubricating oil). TPH is analyzed similar to the Light group described earlier in the "Determination of Petroleum Hydrocarbon in Water for the Decommissioning of Contaminated Sites", but the extractable range is extended to pentacontane by the use of high temperature gas chromatography. The recovery for the entire range of TPH is 80% with a method detection limit of 1 mg/L (ppm). This technique will allow the identification of the petroleum product throughout the stated carbon range.

Current Status

Both methods are near completion as of February, 1999 and will be available for use at the facility early next fiscal year.

C. Collaborative Projects

The projects described in this section are ones which are done in collaboration with external researchers, where the level of effort required by LSB staff is somewhat less than generally required for a full R&D project as described in the previous sections. Collaborations can take place with other government staff, academic researchers, or with the private sector. One additional collaborative project – *LC-MS/MS Determination of Nonylphenol Ethoxylates* – was described in Section A of this Report.

I. Analysis of PM_{10} Particulate for B(a)P

LSB Study Team:	Renee Luniewski & Dan Toner Mass Spectrometry/ Volatiles Section; Kirsten Burling, Physical Chemistry & Litigation Section
Collaboration with:	Dan Orr, Environmental Monitoring and Reporting Branch; Neil Buonocore & Gerald Diamond, Operations Division

The feasibility of collecting B(a)P data from PM10 quartz filters verses the current PAH sampling method (Teflon coated glass fiber filter + XAD) was investigated. The objective, as outlined in the "Air Monitoring Strategy for ESSD" (Sept.97), was to streamline existing operations, as well as propose the use of B(a)P as a surrogate measurement for total PAH toxicity assessment.

Co-located samplers were set up at three stations for a 10 week period (July 22 to Sept.20/98). Although results indicate a strong co-relation between the two sampling methods, the B(a)P levels obtained from the PM10 filter were significantly lower (1:3) than the levels obtained from the current PAH method. This proved unacceptable for sampling sites involved in abatement and/or compliance monitoring. Further investigation would be required to determine the particle size factor, vapor phase contribution, and filter collection efficiency to establish all the B(a)P reported is collected as particulate. The use of B(a)P as a surrogate measurement for total PAH toxicity assessment is subject to approval from the regions.

II. Development of a Certified Reference Material

LSB Study Team:	Sathi Selliah, Eric Reiner
Collaboration with:	Maureen Leaver, CANMET

A decade ago, further improvements in the accuracy of quantitation of ultra-trace organic pollutants in real environmental samples was hindered by the lack of real-matrix certified reference materials (CRMs). One of the difficulties was finding a contaminated area where the level of pollution was at a low but measureable concentration, and contained a number of analytes of interest. During routine testing, a source of sediment was found that contained a wide variety of different chlorinated dibenzo-p-dioxins (CDDs), dibenzofurans (CDFs), polycyclic aromatic hydrocarbons (PAH), trace metals, and other compounds of interest.

Several kilograms of the material were taken from this site and processed by CANMET using International Organization for Standardization (ISO) guidelines. The homogeneity assessment of the material is complete and the task of assigning reference values to the analytes of interest has begun. The complete certification process will take about 2-3 years.

D. Education & Training

Education and training programs are necessary to achieve the Branch goal of ensuring a province-wide analytical laboratory system that delivers readily available and acceptable quality testing in Ontario. In 1998, the workshop on Polynuclear Aromatic Hydrocarbons (PAH) not only addressed this need, but also covered the entire PAH issue including why they are important environmental contaminants – the workshop was thus aimed at the needs of the users of PAH monitoring data in addition to the analyst. The other major education activity of LSB related to the new Partners in Air program.

I. PAH Workshop

Some 60 delegates registered for a 1-day seminar about the sources, toxicity, environmental fate, and laboratory analysis of the polycyclic aromatic hydrocarbons (PAH), held on Wednesday, October 28. The seminar was directed principally towards the users of PAH data, and therefore explained why these compounds are of concern, where they may be found in the environment, and how they are measured.

Professor Brian McCarry from McMaster University began by describing the properties of PAH, their origins, and where they are found in the environment. PAH can be formed from a number of combustion processes, and are ubiquitous. Bryan Leece from the MOE Standards Development Branch then gave an overview of PAH toxicity and risk assessment. William Gizn (MOE, Phytotoxicology Section) explained how sites suspected of PAH contamination are investigated, followed by David Boomer (MOE laboratory) , who discussed measurement uncertainty. Eric Reiner and Ann Jones (MOE laboratory) concluded the seminar by showing how high quality analytical data are generated. At the conclusion of the seminar, Sathi Selliah (MOE laboratory, Quality Management Unit) described a round-robin study organized for laboratories to assess their PAH analytical capability.

II. Science Experiments to Support Partners In Air Program

The Partners in Air (PIA) program was developed by the Ministry of Environment to create awareness of air pollution issues by designing pollution monitoring activities for senior high school students. This pilot project was initiated with 12 high schools across Ontario, linked through a world wide web site. Monthly monitoring of metals in air through analysis of lo-vol filters and moss bags was described earlier in this report, as a semi-quantitative metals method was developed for these PIA sample types. In addition, a sampling and analysis experiment was developed in which coloured dots of paper were used to simulate different types of pollutants in an environmental matrix (air, water, or soil). After mixing the dots and grabbing a sub-sample, the amount or "concentration" of each different colour can be estimated, which is analogous to how real-world sampling and analysis is performed. Other experiments to illustrate principles of environmental analysis are being developed. A workshop for teachers in PIA schools was held March 6.

E. LSB Seminar Series

In the fourth year of the LSB Seminar Series, speakers were drawn from government, academia, and private companies. A wide range of topics were covered, from uncertainty in chemical measurement to the determination of endocrine disruptors to the analysis of metals in tree rings. This year, private-sector environmental laboratories were notified of specific seminars expected to be of interest to them, and considerable interest in these seminars was shown. Descriptions of the 1998 seminars are given below:

I. Guide to the Use of Uncertainty in Measurement
David Boomer (MOE-LSB) and Emilia Lugowski (Brock University)

Conventional analytical chemistry training discusses the precision and accuracy of measurements, but in recent years the concept of *uncertainty* has become an important way of characterizing the quality of results. The International Organization for Standardization (ISO) has published a guide – *Guide to the Expression of Uncertainty in Measurement* – that discusses in detail recommendations for how this should be performed. In this seminar, David Boomer described the issue, and the importance of determining the uncertainty of a measurement. Emilia Lugowski then gave a guided tour of the *Guide*, and explained how the process works. About 40 LSB and external staff attended this seminar on January 30.

II. Screening Method for Pesticides and Endocrine Disrupting Chemicals
James D. McCurry, Hewlett-Packard Company

On May 21, over 30 LSB and other MOE staff attended a seminar by Dr. James McCurry of Hewlett-Packard Company (USA), concerning new gas chromatography (GC) techniques for the determination of pesticides and endocrine disrupting chemicals. Key to these new methods is a concept called retention time locking, which allows an analyst to reproduce a GC method so accurately that analyte retention times are extremely predictable. A database has been developed that contains more than 567 pesticides and potential endocrine disrupting chemicals along with their 'locked' retention times under specific GC conditions. When combined with selective detection by using either a GC-MS, or by calculating a GC peak's elemental ratios by using an

atomic emission detector, the technique provides a rapid and powerful screening tool for pesticides and selected endocrine disrupting chemicals.

III. Current Topics in Environmental Gas Chromatography Frank Dorman and Gary Stidsen, Restek Corporation (Chromatographic Specialties Inc.)

Two specialists from Restek Corporation, Drs. Frank Dorman and Gary Stidsen, spoke to over 40 LSB and private sector analysts on November 5. Their presentation covered some of the latest developments in environmental gas chromatography (GC) including: PCB analysis, chlorinated pesticide and herbicide analysis, endocrine disruptors, and GC techniques such as large volume injections, fast GC, and new columns. Restek has developed a new method for the isomer-specific determination of about 145 PCBs by dual-column GC-ECD. Advantages of application-specific stationary phases were highlighted, and how such phases were developed was discussed. The seminar concluded with a discussion on the new developments in GC that are expected in the next few years.

IV. Advantages of Environmental Surface Analysis Techniques: The Great Tree Ring Anomaly; R.R. Martin, University of Western Ontario

Surface analysis techniques can be used for environmental detective work in a way that conventional instrumental techniques cannot. Tree ring analysis (dendroanalysis) is one example of an application where simple bulk sample analysis methods fail to give very much useful information. Surface techniques, however, can determine the concentrations of metals in adjacent tree rings, which are alleged to contain a record of past pollution events. Professor Ron Martin discussed this application on November 17, and presented compelling evidence that the distribution of metals he studied in tree rings was randomized to a sufficient extent that past pollution events could not be accurately predicted by dendroanalysis.

Publications, Presentations and Methods - 1998 Laboratory Services Branch

A. Publications

1. P.W. Crozier, J.B. Plomley and L. Matchuk. *The Trace Level Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Water Using Solid Phase Extraction and Gas Chromatography-Ion Trap Mass Spectrometry.* Proceedings of *Enviro*Analysis; the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Ontario **1998**, 89-95.

2. J-P. F.P. Palmentier and V.Y. Taguchi. *The Determination of Taste and Odour Compounds in Water using Ambersorb 572 and High Resolution Mass Spectrometry.* Proceedings of *Enviro*Analysis; the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Ontario **1998**, 123-127.

3. M. Pitcher, S. Lemanik, and P. Yang. *The Determination of Organochlorine Pesticides, Polychlorinated Biphenyls (PCB's) and Other Chlorinated Organic Compounds in Water by Hexane Microextraction Gas Chromatography-Electron Capture Detection (GC-ECD).* Proceedings of *Enviro*Analysis; the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Ontario **1998**, 129-134.

4. L. Matchuk, J. Fracassi, B. Ali, and P. Yang. *Using Solid Phase Microextraction (SPME) for Routine Analysis of Waterborne Triazine Herbicides – An Evaluation.* Proceedings of *Enviro*Analysis; the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Ontario **1998**, 183-187.

5. T.M. Kolic, E.J. Reiner, and K.A. MacPherson. *Chlorinated Dioxins/Furans TEQ Concentrations in Biota Samples: A Comparison of Immunoassay versus GC/HRMS.* Proceedings of *Enviro*Analysis; the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Ontario **1998**, 259-264.

6. R. Brunato, E. Reiner, and T. Chen. *A Fast GC/ECD Congener Specific Method for the Analysis of PCBs in Environmental Samples.* Proceedings of *Enviro*Analysis; the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Ontario **1998**, 209-213.

7. M.J. Powell, R.J. McVicars, and D.W. Boomer. *The Determination of Iodine in Potable Drinking Water by ICP-MS.* Proceedings of *Enviro*Analysis; the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Ontario **1998**, 493-499.

8. S. Selliah and S. Cussion. *A Performance Evaluation Program: Quality System Oversight.* Proceedings of *Enviro*Analysis; the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Ontario **1998**, 463-469.

9. C.L. Raposo. *Quality System Assessments – An Auditor/Auditee's Perspective.* Proceedings of *Enviro*Analysis; the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Ontario **1998**, 453-461.

10. E.J. Reiner, T.M. Kolic, K.A. MacPherson, V. Khurana, and R. Brunato. *Dioxin and Toxic Organics – Data Quality Objectives and Method Selection.* Proceedings of *Enviro*Analysis; the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Ontario **1998**, 473-479.

11. R. Clement. *A Simple Experiment for Environmental Sampling and Analysis.* Proceedings of *Enviro*Analysis; the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Ontario **1998**, 719-720.

12. M.J. Powell, R.W Bell, D. Sturgis and S. Menichetti. *The Determination of Hexavalent Chromium in Air Samples by Ion Chromatography.* Proceedings of *Enviro*Analysis; the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Ontario **1998**, 559-567.

13. K.A. MacPherson and E.J. Reiner. *Optimization of GC Capabilities for Improved Analyses of PCDDs and PCDFs.* Proceedings of *Enviro*Analysis; the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Ontario **1998**, 97-103.

14. R. Luniewski, B. Kanabe, L. Nasri, P. Hubber, L. Au, P. Yang, and N. Buonocore. *Gas*

Chromatograph/Isotope Dilution Mass Spectrometric Analysis of Airborne Benzo[a]pyrene Using Deuterium and ^{13}C-Labeled Benzo[a]pyrene: A Critical Evaluation. J. Air & Waste Manage. Assoc. **1998**, *48*, 1085-1092.

15. Vince Y. Taguchi, Steve W.D. Jenkins, Patrick W. Crozier, and David T. Wang. *Determination of Diquat and Paraquat in Water by Liquid Chromatography-(Electrospray Ionization) Mass Spectrometry.* J. Am. Soc. Mass Spectrom. **1998**, *9*, 830-839.

16. J-P. F.P. Palmentier, Vince Y. Taguchi, Steve W.D. Jenkins, David T. Wang, Kim-Phuong Ngo, and Don Robinson. *The Determination of Geosmin and 2-Methylisoborneol in Water Using Isotope Dilution High Resolution Mass Spectrometry.* Wat. Res. **1998**, *32*, 287-294.

17. Ray Clement and Bob Burk, Eds.. *Enviro*Analysis: Proceedings of the Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment, Ottawa, Canada, **1998**, 738 pp.

B. Presentations

1. P.W. Crozier, J.B. Plomley and L. Matchuk. *The Trace Level Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Water Using Solid Phase Extraction and Gas Chromatography-Ion Trap Mass Spectrometry*; presented at 2nd Biennial *Enviro*Analysis Conference, Ottawa, Ontario, May 11-14, 1998.

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13. K.A. MacPherson and E.J. Reiner. *Optimization of GC Capabilities for Improved Analyses of PCDDs and PCDFs*; presented at 2nd Biennial *Enviro*Analysis Conference, Ottawa, Ontario, May 11-14, 1998.

14. Vince Taguchi, Steve Jenkins, Patrick Crozier, and David Wang. *Analysis of Diquat and Paraquat in Water by Liquid Chromatography-(Electrospray Ionization) Mass Spectrometry*, presented at 46th ASMS Conference on Mass Spectrometry and Allied Topics, Orlando, Florida, June 2, 1998.

15. *R.E. Clement*, "The Importance of Science Input to Environmental Policy Development", Talk Presented to 3rd Year Undergraduate Students, York University, November 9, 1998.

16. *R.E. Clement*, Mike Shackleton, Tracy Patterson, "Partners in Air Program", Talk Presented at the Science Teachers' Association of Ontario Annual Conference, November 6, 1998, Toronto, Ontario.

17. *R.E. Clement* and Eric Reiner, "Data Quality and Ultratrace Organics Analysis", Invited Talk Presented at the 112th Annual Meeting and Exposition of the Association of Official Analytical Chemists, September 14, 1998, Montreal, Quebec.

18. *R.E. Clement*, "Career Skills for Technical Jobs", Invited Talk Presented at the Annual *Innovations Canada* Conference, June 16, 1998, Etobicoke, Ontario.

19. *R.E. Clement*, "Technical Careers", Invited Talk Presented to A&WMA Students' Conference, University of Toronto, February 1, 1998.

20. *R.E. Clement*, "Preparing for a Technical Career in Science", Invited Talk Presented at University of Western Ontario Environment Graduate Students' Conference, London, Ontario, March 21, 1998.

21. *R.E. Clement*, "Air Quality Issues and Teaching Resources", Invited Seminar Presented to OISE pre-High School Teacher Class, University of Toronto, March 12, 1998.

22. *Eric Reiner, John Mayes, and Rusty Moody*, "Plastimet – Fire and Brimstone", Invited Talk Presented at the LABontario Conference, Toronto, November 19, 1998.

23. *Eric J. Reiner*, "Dioxin and Toxic Organics, Data Quality Objectives and Method Selection" University of Guelph, Department of Chemistry, Departmental Seminar, April 7, 1998.

24. *Eric J. Reiner*, "The Analysis of Dioxin and Toxic Organics in Environmental Samples" University of Toronto, Department of Chemistry, Departmental Seminar, February 12, 1998.

25. E.J. Reiner, T.M. Kolic, K.A. MacPherson, V. Khurana and R. Brunato, "Dioxins and Toxic Organcis - Data Quality Objectives and Method Selection, 30th Eastern Canada Pesticide Residue and Environmental Contaminants Workshop, Guelph, 1998

26. *Eric J. Reiner*, "Analysis of PAHs in Solid Matrices", Presented at the Seminar: *Polynuclear Aromatic Hydrocarbons in Solid Matrices*, Ministry of Health Auditorium, Toronto, October 28, 1998.

C. New Laboratory Services Branch Environmental Analytical Methods

1. Method E3406A: The Determination of Nitriloacetic Acid (NTA) in Aqueous Samples by Automated Ion Chromatography (IC)

2. Method E3407A: The Membrane Filtration Method Using DC Agar for the Simultaneous Detection of Total Coliforms and E. Coli

3. Method E3408A: The Spread Plate Procedure for the Enumeration of Aerobic Heterotrophic Bacteria in Drinking Water

4. Method E3409A: The Determination of Trace Metals in Air by Moss Bag Collection and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

5. E3410A: The Determination of Iodine in Potable Water by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

6. E8003A: The Determination of Hexavalent Chromium in Air by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

7. E3337A: The Characterization of Organic Compounds by Liquid Chromatography (Particle Beam) – Mass Spectrometry (LC(PB)-MS)